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Fundamentals of Barrier Material Development for Beverage Packaging

Introduction

Improvements in packaging materials rely upon fundamental polymer science, since permeation through a barrier polymer layer primarily determines the efficacy of the package [1]. Poly(ethylene terephthalate) (PET) is a widely used barrier material for packaging of foods and beverages. Packaging of juices and flavored drinks (carbonated and noncarbonated) as well as beer are attractive targets that could benefit from better knowledge of sorption and permeation properties of PET. Key challenges in packaging are: reduction of oxygen invasion, flavor scalping, and reduced loss of carbon dioxide in the case of carbonated beverages. Reaching these goals requires a better understanding of the transport properties of flavor/aroma compounds and the effect of the presence of such molecules on the transport of carbon dioxide and oxygen. Numerous studies are available on pure component transport, but little work has been done on multi-component transport, particularly with a gas and organic vapor mixture. Moreover, it is unwise to extend pure component transport data to predict mixed component transport without careful validation. Both competition and plasticization effects are expected to change the transport properties in a mixture, thereby emphasizing the need for multi-component studies. Analysis of PET properties is further complicated by the presence of orientation and crystallinity which suggests the need for examination of different morphologies for appropriate comparison and prediction.

Specific Objectives

Overarching Goal

- To determine the effect of flavor molecule/simulant on the transport of gases in different morphologies of typical of realistic barrier polymers

- To develop a framework for interpretation and prediction of multi-component transport such that it can be extended to novel barrier materials

One of the challenges in this work has been the identification of a suitable system which can be used to study the effects of organic compounds on transport of gases. Methanol has been chosen as a *model compound* to be used for the multi-component gas/vapor studied and poly(ethylene terephthalate) (PET) has been selected as the model barrier polymer. Thus, the objectives defined for this research are:

Objective 1: *To study the sorption and transport properties of methanol in PET and investigate the differences in transport properties with changes in morphology*

Objective 2: To study *multi-component permeation of CO_2, O_2 and methanol at different activities of methanol in amorphous, annealed and non-annealed, oriented PET*

Objective 3: *To develop a framework within which the observations of objective 2 can be interpreted and extended for the prediction of transport properties of similar systems*

Summary of Conclusions

In pursuit of the overall objective, a system was designed to perform multi-component permeation studies, prepare custom feeds and analyze the permeate. Methanol was identified as suitable system to model the effect of flavor components on transport properties. Its polar, interacting nature and diffusion coefficient of the order of 10^{-10} cm^2/s make it a good flavor molecule simulant with which, permeation experiments can be performed in a reasonable time frame. The equilibrium sorption isotherm and sorption kinetics of methanol have been measured in PET for the first time. Pure methanol vapor equilibrium uptake and sorption kinetics were obtained in different morphologies of PET, namely an amorphous, and an annealed and non-annealed, biaxially oriented semicrystalline film. Crystallinity was found to suppress the extent of swelling, and annealing further reduced the swelling effects. Methanol isotherm shows dual mode sorption effects at low activities and swelling at high activities. These differences in the sorption behavior may lead to different permeation responses of the gas at high and low activities of the vapor. This system therefore retains all the complexity that a real package might encounter.

Pure gas, mixed gas and gas/vapor permeation was performed. Pure gas results were used to obtain the dual mode model parameters for CO_2 and O_2 sorption and transport. The dual mode model has been extended for prediction of multi-component transport. The parameters were therefore, used to predict the transport properties of the gases in mixture.

The major observations and conclusions from the multi-component transport work are summarized below.

1. Gas permeabilities in a CO_2/O_2 binary mixture with a 90/10 CO_2/O_2 feed at 35°C, total pressure of 110 psia, followed the dual mode model prediction very closely.
2. Methanol is a swelling agent at high activities and causes large increases in the permeability of O_2 and CO_2 in the activity range of 80-90%. This effect was analyzed within the framework of Fujita's free volume theory [2]. Based on this theory, an expression for permeability is shown in equation 1 [3]. FFV_o is the fractional free volume of the polymer and A_A and B_A are parameters.

$$P_{Ao} = A_A \exp\left(-\frac{B_A}{\phi_a FFV_o}\right) \tag{1}$$

To model the changes in permeability, increase in the fractional free volume of the polymer-penetrant system was evaluated by assuming additivity of volumes. It was proposed that plasticization induced changes in the free volume should be considered only in the equilibrium packed, densified regions of the glassy polymer. This hypothesis is reasonable because plasticization occurs in both rubbery and glassy polymers. The non-equilibrium sites of the glassy polymer are fixed in number and are occupied at low activities itself. Additional sorption occurs only in the equilibrium, densified domains of the polymer. A modified form of the theory was proposed for analysis of plasticization effects to account for the above hypothesis. Free volume increase as function of methanol concentration was modeled to obtain the value of the parameter B_A for O_2 and CO_2. The value of B_A obtained for O_2 and CO_2 in PET is very different from that proposed by Park and Paul [4] who mostly consider high permeability polymers. This suggests that apart from the total fractional free volume, other factors such as the distribution of free volume, chain cohesive density and rigidity may also play an important role in determining the transport properties. Better understanding of these parameters will provide a tool towards development of novel materials.

3. It was found that there exists a critical concentration of methanol in the amorphous phase of a sample at which the gas permeability shows an upturn. However, at

present, there is no understanding of why this concentration is penetrant dependent, and how its value may be predicted for larger flavor molecules.

4. At low and intermediate activities, the influence of both, plasticization and competition is evident in the O_2/MeOH system, and large enhancements in the permeability are not observed. Despite being below the critical concentration level, methanol is able to induce some conditioning of the polymer which leads to enhancement in the permeability of the amorphous and non-annealed films. These effects do not fit the free volume theory and hence, an extended form of the dual mode model has been used to estimate increase in the diffusivity of the gas at these activities.
5. The ternary system of CO_2/O_2/MeOH system highlights the need to investigate the possibility changes not just in the fractional free volume of the polymer induced by methanol, but also the need to understand the change in distribution of free volume and how it may be accessed by different gases. CO_2 is found to depress below the dual mode level in the amorphous film and oxygen permeability is also lower than was found in the case of O_2/MeOH
6. Crystallization and annealing of the polymer sample suppress the swelling and plasticization effects at the low and high activities. However, residual stress was found to be detrimental to the overall performance of the polymer as sorption induced stress relaxation occurs at intermediate methanol activities of 60% and leads to enhanced gas permeability. However, crystallinity offsets the above effect by preventing the ultimate increase in permeability at high activities beyond that of the purely amorphous sample. However, from a packaging standpoint, since the bottle is blow molded and may have residual stresses, a swelling penetrant at intermediate activities may lead to loss in the barrier properties.

References

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